THE INFRA-RED SPECTRUM OF BORON TRIFLUORIDE

By

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A DISSERTATION

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The Infra-Red Absorption Spectrum of Boron Trifluoride

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The infra-red absorption spectrum of BF_3 has been studied under high resolution from 400 cm^{-1} to 3000 cm^{-1}. The active fundamentals ν_2, ν_3 and ν_4 and the overtone $2\nu_3$ have been observed. The parallel fundamental ν_2 has been partially resolved and the value of the moment of inertia A found to be 79×10^{-40} g cm^2. The B−F distance is 1.29×10^{-8} cm. The isotope effect due to the two isotopes of boron was observed in all bands. The appearance of the unresolved bands ν_4 and $2\nu_3$ is shown to be greatly influenced by the interaction between vibration and rotation.

INTRODUCTION

FOR the past several years the molecular structure of boron trifluoride has been a subject of research by several groups of investigators. The vanishing permanent electric moment[1] and the evidence from electron diffraction experiments[2] indicate that the equilibrium

[1] Linke and Rohrmann, Zeits. f. physik. Chemie **41**, 109 (1937).
[2] H. Levy and L. O. Brockway, J. Am. Chem. Soc. **59**, 2085 (1937).

configuration of the molecule may be described as an equilateral triangle with the fluorine atoms at the corners and the boron atom at the center and in the same plane.

The Raman spectrum was first reported in 1936 by Anderson, Lassettre and Yost.[3] * It was re-examined in 1938 by Yost, DeVault, Anderson and Lassettre[4] and the conclusion reached, "The only line that is certainly present in the Raman Spectrum of BF_3 is the strong one at 888 cm^{-1}. The band at 439–513 cm^{-1} is probably due to BF_3 since it appears in experiments that differ both in technique and method of preparation of the compound." The high frequency line they assigned as the completely symmetrical vibration ν_1, the low frequency band as ν_4.

In 1937 Bailey, Hale and Thompson[5] reported the infra-red spectrum of the gas from 10,000 to 600 cm^{-1}. They observed thirteen bands in this region, the strongest five being at 1501, 1448, 722, 1370 and 2927 cm^{-1}. They called the first two of these an isotopic pair due to the perpendicular fundamental ν_3. The band at 722 cm^{-1} they assigned to the parallel vibration ν_2, but they were not able to resolve it into the expected isotopic doublet.

Since the low frequency fundamental had not been definitely located the spectrum was not complete and, in the published data, certain inconsistencies appeared. The most noticeable of these involved the strong band at 1370 cm^{-1}. The present research was undertaken in hope that the low frequency fundamental might be located and some of the known bands more completely resolved.

Experimental

The spectrometer has been described by Hardy.[6] By using an echelette grating with 800 lines per inch in the first order and one with 360 lines per inch in the second order, the region of investigation was extended to 378 cm^{-1}.

The BF_3 was prepared by the reaction:

$$6H_2SO_4+3KBF_4+B_2O_3 \rightarrow 3K_2SO_4+3H_2O+8BF_3.$$

The reaction chamber was copper, connected by a copper tube to a copper trap in a freezing mixture of alcohol and dry ice, to freeze out any water or HF which might be formed.

Since BF_3 prepared in this manner is generally contaminated with SiF_4 or is likely to become so when in contact with glass, a sample of the latter gas was prepared by the following reaction.

$$CaF_2+H_2SO_4 \rightarrow CaSO_4+2HF$$
$$4HF+SiO_2 \rightarrow SiF_4+2H_2O.$$

The generating apparatus was identical with that used in the preparation of the BF_3 except that the copper trap was kept in a freezing mixture of rock salt and ice.

The use of H_2SO_4 in these reactions is likely to result in the formation of SO_2 and absorptions due to this molecule have been observed in both samples of gas. The spectrum of SO_2 is being studied in this laboratory at present, and the observations have been available for comparison with the data here reported.

Results

Seven bands were observed that can be definitely assigned to BF_3. Accurate intensity measurements were not made but a qualitative idea of the intensity may be gained from the product of the cell length by the gas pressure for any observation which we shall designate as k.* The smaller the value of k for satisfactory observations on a certain band, the more intense the band must be.

The 480 cm^{-1} Band

The lowest frequency band observed was a fairly strong one centered at very nearly 481 cm^{-1}. The envelope is reproduced in Fig. 1 and resembles that of a parallel band. The best results were obtained with $k=42.5$. The strong central region was examined at several different pressures and proved to be a doublet, the frequency of the components being 480.5 and 482.1 cm^{-1}. Several lines in this region due to the rotation spectrum

[3] T. F. Anderson, E. N. Lassettre and D. M. Yost, J. Chem. Phys. **4**, 703 (1936).

* The normal modes of vibration of the coplanar AB_3 molecule are given in this paper.

[4] D. M. Yost, D. DeVault, T. F. Anderson and E. N. Lassettre, J. Chem. Phys. **6**, 424 (1938).

[5] C. R. Bailey, J. B. Hale and J. W. Thompson, Proc. Roy. Soc. **161**, 107 (1937).

[6] J. D. Hardy, Phys. Rev. **38**, 2162 (1931).

* The unit for k will be one cm cell length by one cm Hg pressure.

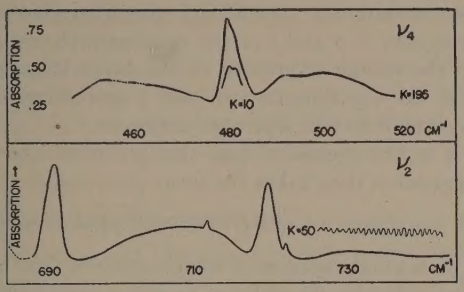

FIG. 1. Envelopes of the perpendicular band ν_4 and the parallel band ν_2. Value indicated as K=195 showed by K=19.5.

of water interfered with the observations at certain points on the envelope. These regions are shown by broken lines in Fig. 1. This band is assigned as the low frequency fundamental ν_4.

The Region from 690 cm^{-1} to 743 cm^{-1}

An absorption was observed which extended throughout this entire region and probably forty or fifty wave numbers farther on the low frequency side, where the absorption due to atmospheric CO_2 made observations uncertain. In the region which was examined the strength of the absorption varied greatly, and the band had to be studied at several different pressures; in consequence Fig. 1 does not give the correct intensity relations. Absorption could be detected with $k=8$ on the zero branches, and for certain regions the best value was $k=120$. Two strong zero branches were observed at 691.50 cm^{-1} and 719.70 cm^{-1}. A much weaker line was observed at 711.50 cm^{-1}.

Twenty-four fine structure lines due to rotation were observed in the interval between 726 cm^{-1} and 744 cm^{-1}, using $k=50$. They correspond to values from 10 to 33 of the ordinal number m counted from the band center, as indicated in Table I. The computed frequencies are obtained from the formula

$$\nu = 719.80 + 0.71m - 0.0001m^2.$$

This absorption is assigned as ν_2, the active parallel vibration, with two zero branches due to the isotope effect. The line at 711.5 is probably the zero branch of the upper stage transition $\nu_2 \rightarrow 2\nu_2$.

The bands at 1446 and 1500 cm^{-1}

These bands lie in a region where water vapor absorption interfered greatly with the observations. The results are shown in Fig. 2. The solid lines represent apparent absorptions and the broken lines represent background. Interference due to water vapor was least on the low frequency side and the center of one band may be located at 1446.3 ± 1.0 cm^{-1}. An attempt was made to resolve the rotational structure but without success. The other band was located near 1500 cm^{-1} where conditions are very unfavorable and no great accuracy can be claimed for the position of the band center. The best value appears to be 1497 cm^{-1}.

These two bands are the most intense in the BF_3 spectrum. Most of the observations were made with $k=2.5$ for the low frequency band and $k=10$ for the high frequency band. The bands are assigned as the high frequency perpendicular fundamental ν_3.

The only combinations observed were the first overtones of ν_3. The envelopes of these bands are quite different from those of the fundamentals, and will be discussed later. The band centers are at 2904.0 and 3009.0 cm^{-1} where, in both cases, there is a strong absorption maximum about 5 cm^{-1} wide. On the high frequency side there are

TABLE I. *Observed and computed frequencies for part of the ν_2 band.*

m	ν_{OBS}	ν_{COMP}	$\nu_c - \nu_0$
10	726.80	726.89	0.09
11	727.55	727.61	0.06
12	728.20	728.31	0.11
13	729.06	729.02	−0.04
14	729.84	729.72	−0.12
15	730.62	730.43	−0.19
16	731.26	731.13	−0.13
17	731.95	731.84	−0.11
18	732.60	732.55	−0.05
19	733.34	733.25	−0.09
20	734.01	733.96	−0.05
21	734.69	734.67	−0.02
22	735.40	735.37	−0.03
23	736.09	736.03	−0.06
24	736.82	736.78	−0.04
25	737.44	737.49	0.05
26	738.18	738.19	0.01
27	738.93	738.89	−0.04
28	739.51	739.59	0.08
29	740.31	740.30	−0.01
30	740.92	741.01	0.09
31	741.64	741.70	0.06
32	742.37	742.41	0.04
33	743.05	743.01	−0.04

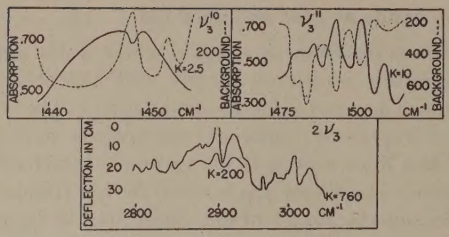

FIG. 2. Observed absorption due to ν_3 and $2\nu_3$.

less intense maxima extending over a much wider frequency range and centered at 2927.0 and 3032.3 cm^{-1}. On the low frequency side there is another broad region of absorption which is weaker than either of the others. An estimate of the center of this region cannot be made with any great accuracy from the present data.

Throughout the whole region there are lines which stand out prominently above the envelope of the bands. These lines are listed in Table II and for each line an integer is given which indicates very roughly the intensity and is primarily for identification. There is no regularity in the spacing of the lines and the intervals between them are so large as to seem improbable for BF_3. They may be due to a contaminant, since BF_3 attacks the stopcock grease and the lacquer used in sealing the cells, and a compound containing hydrogen could easily be formed which would perhaps account for them. For the stronger of the two absorptions given in Fig. 2 $k=760$, for the weaker $k=190$.

In general the results agree reasonably well with those obtained by Bailey, Hale and Thompson, although we were unable to locate several of the weak maxima they describe, and found that the strong one reported by them at 1370 cm^{-1} was due to a contaminant (SO_2).

INTERPRETATION

The normal coordinate treatment of the AB_3 molecule has been carried out by several authors.[7-9]

Following the general method introduced by Rosenthal and by Johnston and Dennison, we use as internal coordinates the Cartesian coordinates x, y and z of the A atom with respect to the center of gravity of the three B atoms, and the coordinates ξ, η and ζ introduced by Bjerrum[10] for the triatomic molecule.

For the coplanar case the potential energy expression then takes the form

$$V=a(x^2+y^2)+b(\eta^2+\xi^2)+2c(x\xi+y\eta)+dz^2+e\zeta^2.$$

The normal coordinate solution shows that the perpendicular frequencies ν_3 and ν_4 are doubly degenerate; consequently for one molecule there are not enough observable frequencies to determine the values of the constants a, b and c. However when the A atom has two isotopes all the constants may be evaluated since the treatment is completely unchanged, and enough natural frequencies are obtainable.

The fundamental frequencies as observed are

	$B^{11}F_3$	$B^{10}F_3$
ν_1	888	888
ν_3	1446	1497
ν_2	691.5	719.8
ν_4	480.5	482.1

The force constants have the values

$$a= 10.5 \times 10^5 \text{ dynes/cm}$$
$$b= 3.90\times 10^5$$
$$c=\pm 3.55\times 10^5$$
$$d= 2.58\times 10^5$$
$$e= 8.75\times 10^5.$$

Moments of inertia

For a symmetric molecule the spacing of the fine structure lines in a parallel band is given by

$$\Delta\nu=h/4\pi^2A,$$

where A is the moment of inertia about a line perpendicular to the axis of symmetry. From the data of Table I $\Delta\nu=0.71$ cm^{-1}. The corresponding value of A is 79×10^{-40} g cm^2, and the B–F distance is 1.29×10^{-8} cm. This agrees very well

TABLE II. *Prominent lines in the $2\nu_3$ bands.*

2800.0	3	2883.0	1
2808.3	2	2890.2	1
2829.3	5	2965.0	5
2845.0	4	2982.9	5
2866.2	2	2998.5	2

[7] J. E. Rosenthal, Phys. Rev. **47**, 235 (1935).
[8] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).
[9] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934).
[10] N. Bjerrum, Verh. d. D. Phys. Ges. **16**, 737 (1914).

with the distance 1.30×10^{-8} cm obtained by electron diffraction.

For a coplanar molecule the moment about the symmetry axis is equal to $2A$, i.e., $C=158\times10^{-40}$ g cm^2. It is to be kept in mind that this is not a measurement obtained directly from the experimental data.

Vibration-rotation interaction

Johnston and Dennison[8] in their study of the vibration-rotation interaction in NH_3 give an expression for the spacing between zero branches of the subsidiary bands due to a perpendicular transition. In the case of a coplanar molecule AB_3 this expression becomes

$$\Delta\nu=\frac{h}{4\pi^2A}\left\{\frac{1-\zeta}{2}-1\right\}.$$

The ζ, which may be different for different perpendicular bands, is a function of the masses, the natural frequencies, and the potential constants. All these have been determined from the experimental data, and the ζ for the different bands may be computed. From the values of ζ and of the moment of inertia A it is possible to compute, by means of the above formula, the spacing to be expected in a perpendicular band due to a transition starting from the ground state (for which $\zeta=0$). These values are

	ζ	$\Delta\nu$
ν_4	−0.86	0.052
ν_3	0.86	0.706
$2\nu_3$	−1.72	0.267

The shape of the envelope for ν_4 and $2\nu_3$ is now explained. Due to the large interaction the interval between the centers of the subsidiary bands becomes very small compared to the spacing in the subsidiary band itself, and the envelope of the perpendicular band resembles that of a parallel band.

Isotope effect

It has been pointed out that if more than one isotopic form exists for the atoms of a compound, the molecules with different isotopes will have the same force constants but different reduced masses, and thus will have different natural frequencies.

For the parallel frequency of BF_3 the case is especially simple and the relation between the frequencies and the reduced masses is

$$\nu_2^{10}/\nu_2^{11}=(\mu_{11}/\mu_{10})^{\frac{1}{2}}.$$

Substituting into this the known quantities we obtain

$$1.0409=1.0411.$$

In the case of the perpendicular bands the relation is

$$\nu_3^{10}\nu_4^{10}/\nu_3^{11}\nu_4^{11}=(\mu_{11}/\mu_{10})^{\frac{1}{2}}$$

and substitution of the measured frequencies gives

$$1.0397=1.0411.$$

This is not so satisfactory, but, as was pointed out above, the center for ν_3^{10} could not be very accurately determined. If this frequency were taken to be 1500.7 cm^{-1} instead of 1497 cm^{-1}, the above relation would be satisfied exactly. Thus 1500.7 is perhaps a more reliable value than the one based upon observational data. This change would not affect the third significant figure in the computed force constants. It is interesting to note that substitution of the values given by Bailey, Hale and Thompson in the frequency relation gives

$$1.0407=1.0411.$$

Their values are somewhat lower than ours, but the ratios are practically the same.

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